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STORABILITY OF PREPARED RAW SURIMI*

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Received October 14, 1982

Introduction

Raw surimi is in a great many cases better than frozen surimi in terms of the manufacturing process and product quality of paste products. Hence, those hoping for its distributability year-round from Hokkaido to Kyushu are by no means few. The present situation, however, is that its quality deteriorates in an extremely short period, making distribution during periods of high temperature impossible.

Raw surimi when frozen deteriorates markedly in kamaboko [fish-cake] formability.[1)] Therefore, in order to enhance the storability of raw surimi, up to now methods have been examined to store it in the unfrozen state near -3°C by adding sodium chloride and ethyl alcohol, etc., to raw surimi to lower its freezing point.[1-3)] It has been confirmed that raw surimi to which has been added

* [Translator's note: Surimi = minced (fish) flesh]

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1% sodium chloride or 3% ethyl alcohol will not deteriorate in kamaboko formability from six days of storage at -3°C.[3] Nevertheless, because there are technical difficulties in maintaining -3°C during storage and transportation, it would be desirable to lower the freezing point of surimi further, whereby the possibility of storage for ten days or even more may be hoped for.

In the present experiment, the additives to lower the freezing point of raw surimi were grouped according to chemical structure, and the effect of the type and added concentration of these test agents on lowering the freezing point for raw surimi was investigated. Also, the effect on the storability of raw surimi of the additives selected from each group was examined from the aspect of the Ca^{2+}-ATPase activity and protein solubility of actomyosin.

Experimental Material and Methods

1. Experimental material

Live dabs (Limanda yokohamae) were obtained at Tokyo's Tsukiji Central Fish Market and used.

2. Method of preparation of raw surimi

After spot-killing the fish, they were filleted and the fillets were finely chopped up with a cleaver, and then blanched three times with five parts of ice water. After that, thorough dehydration was carried out with a double layer of gauze, and then finely chopping up again, this was ground down in a cooled mortar. Measuring the water content of part of this surimi, the water content in the surimi was adjusted to 83%. Next, sodium chloride and sodium acetate as binary electrolytes, saccharose, glucose and fructose as sugars, sorbitol and mannitol as sugar-alcohols, glycine and monosodium glutamate as amino acids, and ethyl alcohol, ethylene glycol, glycerin and propylene glycol as alcohols were added to a fixed amount of this surimi so as to form a prescribed concentration, grinding this together to make the test samples. Hereafter, the raw surimi with these additives added will be referred to as blended raw surimi.

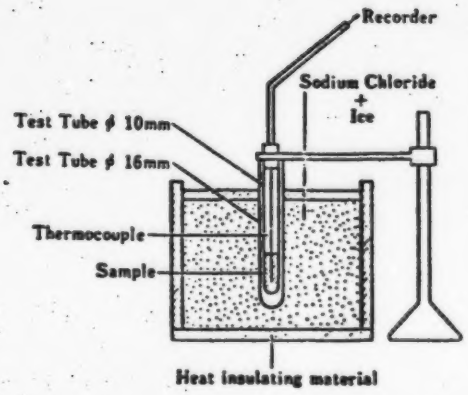

Fig. 1 An apparatus for measuring depression of freezing point.

3. Method of measurement of the freezing point of blended raw surimi

Fig. 1 shows the apparatus used for measurement. Placing the blended raw surimi in a test tube of 10 mm inner diameter and inserting a copper-constantan thermocouple therein, this was put into a test tube of 16 mm inner diameter cooled by crushed ice and sodium chloride. The resultant change in the electromotive force of the thermocouple was plotted with a Hitachi Model 056 desk-top recorder. [122] For the datum point a commercially available specialized pot (Gold Junction Unit Model 612 Chino) was used. The relationship between electromotive force and

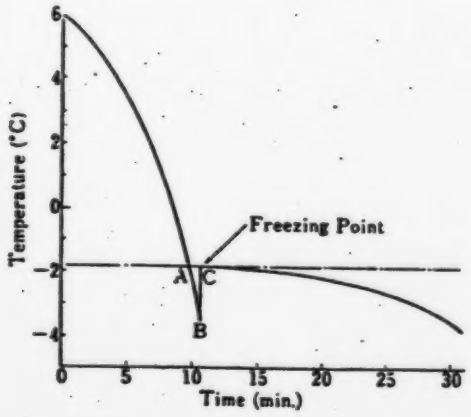

Fig. 2 Freezing curve of raw surimi.

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temperature, as a result of measurements at several different temperatures using a Beckmann thermometer, was such that the change in electromotive force was 0.042 mV per 1°C. The freezing point of raw surimi, as shown in Fig. 2, was taken to be point C appearing after the supercooling phenomenon occurring between A-B. The depression of the freezing point of blended raw surimi was determined by subtracting the freezing point of untreated raw surimi from the freezing point of blended raw surimi.

5. Method of preparation of actomyosin

The method of Arai[4] was followed.

6. Method of measurement of Ca^{2+}-ATPase activity

The method of Arai[5] was followed. The measurement of the protein level was by the buret method.[6]

7. Method of measurement of protein solubulity[7]

Homogenizing 2 g of blended raw surimi together with 35 mL of a 5% NaCl solution, this was subjected to 30 minutes of centrifugal separation at 8,000 x g, and the nitrogen level of the supernatant liquid was measured by the Kjeldahl method. Also, the total nitrogen level in 2 g of blended raw surimi was likewise measured by the Kjeldahl method, and expressing the nitrogen level in the supernatant liquid relative to the total nitrogen level as a percentage, this was taken as the protein solubility.

Results and Discussion

1. Effect of various blended additives on lowering the freezing point of raw surimi

The depression of the freezing point of blended raw surimi corresponding to the added concentration of the freezing point depressant is shown in Table 1. Also, the results of converting the concentration of the additives to molar concentration corresponding to an 83% water content in raw surimi are shown in Figs. 3-6. Specifically, Fig. 3 shows the case involving binary electrolyte

Table 1 Depression of freezing point of prepared raw surimi

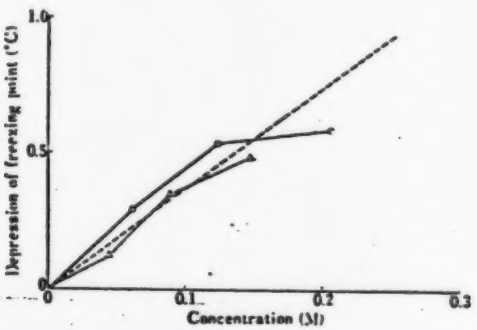
Additives	Concentration (%)	Depression of freezing point (°C)
Sodium Chloride	0.3	0.29
	0.6	0.53
	1.0	0.58
Sodium Acetate	0.3	0.12
	0.6	0.34
	1.0	0.48
Saccharose	0.3	0.12
	0.6	0.17
	1.0	0.67
	5.0	0.91
	10.0	1.43
Glucose	1.0	0.01
	5.0	0.71
	10.0	1.67
Fructose	1.0	0.45
	5.0	1.07
	10.0	1.76
Sorbitol	1.0	0.17
	5.0	1.17
	10.0	1.79
Mannitol	1.0	0.50
	5.0	1.29
	10.0	1.91
Glycine	0.3	0.27
	0.6	0.27
	1.0	0.57
	2.0	0.93
	3.0	1.12
Monosodium Glutamate	0.3	0.10
	0.6	0.12
	1.0	0.36
Ethyl Alcohol	0.3	0.31
	0.6	0.46
	1.0	0.62
	2.0	0.93
	3.0	2.30
Ethylene Glycol	1.0	1.17
	2.0	1.55
	3.0	1.93
Glycerin	1.0	1.02
	2.0	1.38
	3.0	1.67
Propylene Glycol	0.3	0.05
	0.6	0.24
	1.0	0.41

additives, Fig. 4 sugar and sugar-alcohol additives, Fig. 5 amino acid additives and Fig. 6 alcohol additives, respectively.

The depression of the freezing point of raw surimi blended with sodium chloride and sodium acetate, as shown in Fig. 3, can be seen to be in virtual agreement with the depression of the molecular freezing point of aqueous binary electrolyte solution. From this, it would appear that the depression of the

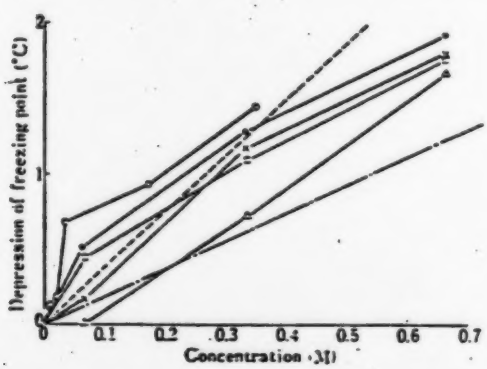
freezing point of raw surimi blended with binary electrolytes can generally be surmised from the molarity of the additives relative to the water content in raw surimi. In other words, because the depression in freezing point is 1.86 when one mole of solute is dissolved in water, with binary electrolytes it becomes double that or 3.72, so this means if the molar concentration of binary electrolytes relative to the water content of raw surimi were multiplied by 3.72, the depression in freezing point of blended raw surimi can be calculated. Now, as

[123]



○ : Sodium Chloride △ : Sodium Acetate
---- : Depression of freezing point of aqueous binary electrolyte solution

Fig. 3 Depression of freezing point of prepared raw surimi blended with binary electrolytes.

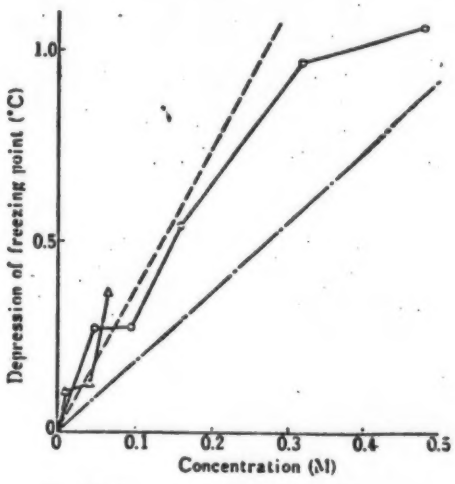


○ : Saccharose △ : Glucose □ : Fructose
× : Sorbitol ● : Mannitol
——— : Depression of freezing point of aqueous binary electrolyte solution
– – – – : Depression of freezing point of aqueous nonelectrolyte solution

Fig. 4 Depression of freezing point of prepared raw surimi blended with sugars, sugar-alcohols, respectively.

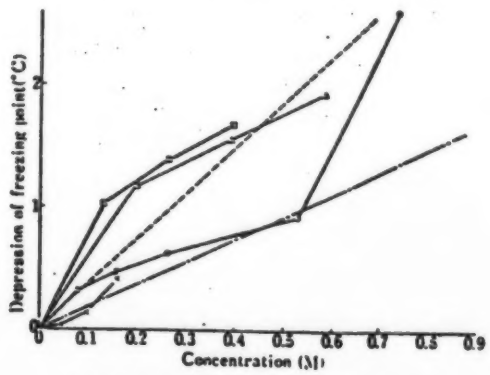
for the additive quantity of sodium chloride, with 1.5% or more the surimi has been reported to set during storage,[3] so that a 1% addition is thought to be the limit.

The depression of the freezing point of raw surimi blended with sugars and sugar-alcohols, as is clear from Fig. 4, is, except for the glucose additive,



○ : Glycine △ : Monosodium Glutamate
——— : Depression of freezing point of aqueous binary electrolyte solution
– – – – : Depression of freezing point of aqueous nonelectrolyte solution

Fig. 5 Depression of freezing point of prepared raw surimi blended with amino acids.



○ : Ethyl Alcohol △ : Ethylene Glycol
□ : Glycerin × : Propylene Glycol
——— : Depression of freezing point of aqueous binary electrolyte solution
– – – – : Depression of freezing point of aqueous nonelectrolyte solution

Fig. 6 Depression of freezing point of prepared raw surimi blended with alcohols.

generally greater than the depression in molecular freezing point of aqueous non-electrolyte solution, with saccharose in particular indicating a freezing point depressive effect greater than that of aqueous binary electrolyte solution. Doing a comparison at the maximum possible additive level of 10%[5] for frozen surimi, the depression in freezing point with the mannitol additive was the greatest at 1.91°C, followed by sorbitol, fructose, glucose and saccharose in that order (Table 1).

The depression of the freezing point of raw surimi blended with amino acids, according to Fig. 5, indicates with both glycine and monosodium glutamate additives at low concentration a depressive effect close to the value for binary electrolyte additive, but with glycine the depressive effect tapers off from around 0.3 M. Now, since both amino acids possess a strong taste-enhancing function, any addition at high concentration is not thought to be desirable from the taste aspect.

The depression of the freezing point of raw surimi blended with alcohols, [124] according to Fig. 6, indicates both ethylene glycol and glycerin exceed the depressive effect of binary electrolytes up to around 0.4 M, whereas with ethyl glycol the depressive effect is low until around 0.5 M. The depressive effect of propylene glycol is virtually consistent with the depression in molecular freezing point of aqueous non-electrolyte solution.

From the foregoing results, it would appear that the effect of alcohols to depress the freezing point of raw surimi increases from monovalence to bivalence to trivalence in that order, but that even a polyhydric alcohol like propylene glycol, if it contains an alkyl group, has no effect on lowering the freezing point.

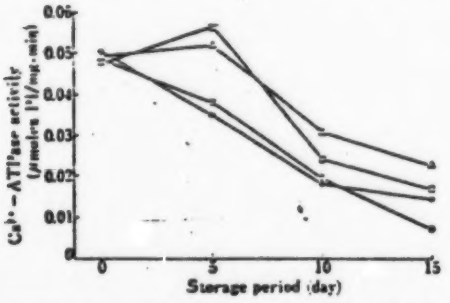
The reason why the depression of the freezing point of raw surimi blended with sugars, sugar-alcohols, amino acids and alcohols shown in Fig. 4, Fig. 5 and Fig. 6 is greater than the depression of the molecular freezing point of aqueous

non-electrolyte solution is thought to be that all of these additives take up the free water in the blended raw surimi due to hydration, as a result of which the molar concentration of the blended material gets raised. The depressive effect on the freezing point of additives with a high hydration capacity may have to be individually measured to ascertain its relationship with the additive concentration.

2. Change in blended raw surimi during storage

Using raw surimi whose freezing point is -1.93°C and preparing blended raw surimi with a 1% addition of sodium chloride, 5% addition of saccharose and 3% addition of ethyl alcohol, this was stored in an unfrozen state at -2°C, and the Ca^{2+}-ATPase activity and protein solubility during storage were measured.

(1) Ca^{2+}-ATPase activity. As shown in Fig. 7, untreated and sodium chloride-added raw surimi kept declining in virtually the same pattern up to the tenth day of storage. By contrast, raw surimi blended with saccharose and ethyl alcohol consistently indicated a higher activity than untreated raw surimi, revealing their effectiveness as blended raw surimi. Particularly after the tenth day of storage, the saccharose blend maintained the highest activity. It is well known that sugars have a suppressive effect on the refrigeration degeneration of actomyosin and exert a pronounced effect on the preservability of



● : None △ : Saccharose □ : Ethyl Alcohol
○ : Sodium Chloride

Fig. 7 Change in the Ca^{2+}-ATPase activity of prepared raw surimi during storage at −2°C.

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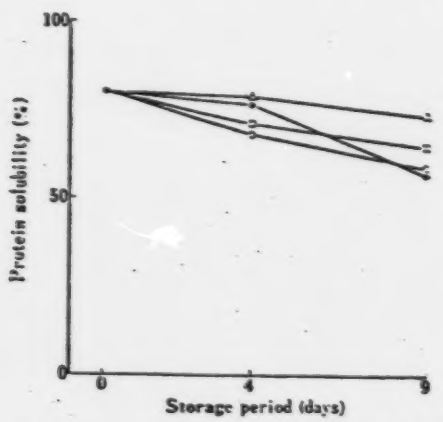
frozen surimi.[9] During the storage of unfrozen blended raw surimi in the present experiment as well, the suppressive effect of sugar on the degeneration of actomyosin is thought to have functioned. On the other hand, with 15 days of storage the sodium chloride blend dropped in activity below the untreated sample. This is thought to be because, even with a 1% addition, by virtue of 15 days of storage setting had progressed, causing actomyosin to degenerate.

(2) Protein solubility. As shown in Fig. 8, in the untreated case there was not much decline up to four days, but thereafter a sudden drop occurred. By contrast, with the saccharose blend not much decline can be seen even after nine days of storage. On the other hand, with the ethyl alcohol and sodium chloride blends there was already a decline by the fourth day of storage.



● : None △ : Saccharose □ : Ethyl Alcohol
○ : Sodium Chloride

Fig. 8 Change in protein solubility of prepared raw surimi during storage at −2°C.

Abstract

Depression of the freezing point and change in the properties of protein storage of prepared raw surimi were investigated and the following results were obtained.

1. Depression of the freezing point of prepared raw surimi blended with binary electrolyte almost agreed with the molecular depression of the freezing point caused by the additives and the moisture in prepared raw surimi.

2. Depression of the freezing points of prepared raw surimi blended with nonelectrolytes differed remarkably at every additive. However, the additives having high hydration capacities lowered the freezing point of the prepared raw surimi.

3. The freezing point of prepared raw surimi blended with alcohols was lowered with the number of hydroxy group. It seems, however, that the polyalcohol containing alkyl-group did not lower the freezing point of prepared raw surimi.

4. In this experiment saccharose was the most effective additive for storage of prepared raw surimi.

[125]

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